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STUDIES ON THE SHRINKAGE PHENOMENON: X. EFFECT OF USING PROCESSING LIQUOR AS HEATING MEDIUM ON THE SHRINKAGE BEHAVIOUR OF SKINS SUBJECTED TO PRETANNING TREATMENTS

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The shrinkage behaviour of skins subjected to pretanning chemical treatments was studied using respective processing liquors as heating media. Compared to the values obtained by using water as heating and recovering medium, the shrinkage temperature (T_s) and area shrinkage (A.S.) of the limed sample were less and those of the pickled sample more; the area recovery (A.R.) of the limed sample was more and of the pickled sample considerably less. Except in the case of the pickled sample which showed a reduction in the (dry) apparent volume on carrying out the shrinkage in either of the heating media, water or processing liquor, no change in the (dry) apparent volume on shrinkage was observed. However, if the samples were not dried, the apparent volume decreased in raw limed and delimed samples. The difference in behaviour between wet and dry samples indicates the non-interference of osmotic swelling with respect to 'dry' apparent volume shrinkage (A.V.S.) measurements. This fact is further supported by the observed wet apparent volume increase on shrinkage of the pickled samples when heated, and very high wet apparent volume on recovery in water, even though the corresponding dried samples showed reduction in the dry apparent volume and no recovery.

The hydrothermal shrinkage behaviour, shrinkage temperature, area and apparent volume changes of skins subjected to pretanning chemical treatments were studied in detail;[1,2] it was observed that the diffusion of chemicals present in the pelt into water influences the hydrothermal shrinkage behaviour.[1] Hence it was considered necessary to compare the shrinkage behaviour of skin samples taken at different stages of pretanning treatments using water and the respective processing liquor as heating media (e.g., limed samples in lime water).

In the earlier[2,3] as well as the present work, the apparent volume changes associated with hydrothermal shrinkage were assessed for dry samples whereas area changes were measured and assessed for wet samples.[1] Hence changes in the apparent volume of wet, non-dried samples were also determined so as to have a better understanding of the changes that take place in thickness during shrinkage, the influence of drying on shrinkage and the extent of influence of processing liquor when used as heating medium on the dimensional shrinkage. Apparent volume shrinkage of dried samples is referred here as 'dry' and that of fresh non-dried sample as 'wet'.

Experimental

The skins were processed following the procedure adopted in our earlier work[1] and the scheme of sampling followed in the earlier studies was also employed in the present work with the following variation.

Pairs of samples marked 1 & 2, 3 & 4, 5 & 6 and 7 & 8 in Fig. 1 of the previous paper[1] were respectively used for testing after soaking, liming, deliming and pickling; the odd-numbered samples were used to study the area and dry as well as wet apparent volume changes in water, and the even numbered samples in the processing liquors.

Before carrying out the wet apparent volume measurements, the samples were blotted uniformly.

Results and discussion

In area and apparent volume shrinkage and recovery values, a large variation was observed but a trend could be determined (Table 1).

It is seen from Table 1 that the use of processing liquor affects the T_s of wet (non-dried) limed and pickled samples. T_s of limed samples is considerably decreased and that of pickled is appreciably increased on using the respective processing liquor as heating medium instead of water. If the samples tested are dried and rewetted, no difference in the T_s of limed samples tested in water

Table 1

EFFECT OF USING PROCESSING LIQUOR ON DIMENSIONAL SHRINKAGE BEHAVIOUR OF SKINS

		Raw	Limed	Delimed	Pickled
(i) *Shrinkage temperature* (°C)					
Wet sample		66 (65)	56 (50)	62 (62)	54 (60)
Dried and rewet sample		70 (69)	67 (68)	68 (68)	56 (64)
(ii) *Wet area shrinkage*					
Average	A.S.	54 (51)	46 (40)	56 (57)	62 (76)
	A.R.	5 (3)	19 (27)	6 (8)	34 (2)
(iii) *Wet apparent volume shrinkage*					
	A.V.S.	20 (23)	38 (44)	20 (23)	- 14* (+ 29)
	A.V.R.	20 (25)	29 (20)	30 (41)	—very high* (1·5)

* Negative sign indicates increase in volume
Shrinkage values of the samples shrunk in the respective processing liquors are given in the parenthesis.

or lime water is observed. But in the case of T_s of pickled samples, the same trend as in the wet samples is maintained though the difference in T_s values is narrowed. The T_s values of dried and rewetted raw, limed, delimed and pickled samples are generally higher than the corresponding non-dried samples though in the case of pickled samples the difference is small.

It may also be seen that the area shrinkage values of limed samples tested in lime water and those of pickled samples in water are less compared to the corresponding values of the samples tested in water and pickle respectively. However, the difference in the area shrinkage values of limed samples tested in water and lime water is less appreciable. But in the case of pickled samples, increase in area shrinkage and decrease in area recovery of pickled samples in pickle are appreciable.

It was reported earlier[2] that there was no change in the dry apparent volume due to shrinkage or recovery in water of raw, limed and delimed samples. It is observed that this apparent volume shrinkage behaviour is not altered when the respective processing liquors are used as heating and recovering media; only pickled samples exhibited a decrease in the apparent volume which is more when tested in water (32% in water and 24% in processing liquor).

In the case of raw, limed and delimed samples, there is a considerable shrinkage in the wet apparent volume on using water or processing liquor as heating medium. While a shrinkage in the wet apparent volume of pickled samples shrunk in pickle is observed, there is an increase in the wet apparent volume on shrinkage and quite an abnormal increase on the recovery of samples in water.

When the limed samples are heated in water for shrinkage, they are subjected to slow deliming influence of water which causes a reduction in H-bond breaking ability of swelling forces. This is responsible for the higher T_s of wet limed samples tested in water compared to those tested in lime liquor. Swelling forces are also responsible for the lowered T_s of pickled samples tested in water compared to those tested in the pickle. As only a negligible quantity of salt is present in soak as well as deliming liquor, there is no appreciable difference in the T_s values of samples either in water or in the respective processing liquors.

Rise in T_s of dried raw, limed, delimed and pickled samples and the absence of any difference in the T_s of dried raw, limed and delimed samples were attributed to the effects of air drying[2] on samples at various stages of pretanning treatments. The absence of difference in T_s of dried and rewetted limed samples in water and lime water can also be attributed to the influence of air drying. When once limed samples are air dried, carbonisation and dehydration of lime take place resulting in poor wettability of dried limed samples. Presence of such dried lime hinders the swelling ability of limed samples in lime water and hence use of lime water as heating medium does not result in the decrease of T_s compared to water as heating medium. Less appreciable difference in area shrinkage values of limed samples tesetd in water or lime water is due to the decrease in swelling during shrinkage, because of reduction in -OH content of the heating medium caused by poor lime solubility[4, 5] and higher ionisation constant of water at higher temperature.[5, 6] The deliming nature of water is thus made less effective when used for carrying out shrinkage; this resulted in less appreciable difference in area shrinkage values of wet limed samples tested in water and lime water. Perhaps this reason also holds good for the absence of any appreciable difference in the wet apparent volume shrinkage values of limed samples in water and lime water. Since -OH ion content is lowered, it consequently reduced the swelling effect with the rise of temperature of lime water or water[5] in the shrinkage experiment. It may hence be said that the lower T_s of wet limed sample in water compared to that of corresponding raw or delimed sample and the still lower T_s of limed sample in lime water is mainly due to the lyotropic effect of lime.[7]

A small decrease in area and a good increase in the wet apparent volume due to shrinkage of pickled samples in water can be attributed to the swelling caused by the dilution of pickle when compared to those of the pickled samples in pickle.

The absence of any appreciable change in the dry apparent volume even though there is a decrease in the wet apparent volume of raw, limed and delimed samples in water or respective processing liquor indicates that apparent volume change caused by the hydrothermal shrinkage in the wet state is nullified by the effects of drying.

A good increase in the wet apparent volume of pickled samples accompanied by a small decrease in area due to shrinkage of wet pickled samples indicates that there is a good increase in thickness during shrinkage when there is a predominant influence of osmotic swelling. Decrease in dry apparent volume of pickled samples shrunk in water or pickle, though there is an increase in wet apparent volume, once again demonstrates the influence of drying on shrinkage behaviour of skins processed. It also shows that osmotic swelling does not interfere with dry apparent volume shrinkage values.

The noninterference or noninfluence of osmotic swelling on dry apparent volume shrinkage is further shown by the poor apparent volume recovery of shrunken dried pickled samples in water in contrast to the good apparent volume and area recovery of shrunken wet pickled samples.

Conclusion

It is concluded that the diffusion of chemicals present in wet limed and pickled pelt into water, the heating medium, influences the shrinkage behaviour of wet samples and not that of dry samples (e.g., dry apparent volume shrinkage). Drying masks the influence of swelling and diffusion on shrinkage temperature as well as apparent volume changes that take place during shrinkage of wet samples.

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